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Thermal Cracking of Sugars for the Production of Glycolaldehyde and other Small Oxygenates

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Abstract: Thermal cracking of sugars for production of glycolaldehyde, a potential renewable platform molecule, in yields up to 74 % with up to 95 % carbon recovered in the condensed product was demonstrated using glucose as the feed. The process involves spraying an aqueous sugar solution into a fluidized bed of glass beads. Continuous operation was shown for more than 90 hours with complete conversion and stable product selectivity. Besides glycolaldehyde, the other identified condensed products were pyruvaldehyde (9 %), formaldehyde (7 %), glyoxal (2 %), acetol (2 %) and acetic acid (1 %). The effects of temperature, glucose feed concentration and type of sugar feedstock were investigated. Cracking the monosaccharides fructose and xylose showed very different product distributions from glucose, but similar carbon recovery. A reaction network in agreement with the main observed products from cracking of monosaccharide sugars is suggested.

With the depletion of fossil resources and environmental concerns over their use, processes utilizing renewable resources are being developed with the aim to supplement, and ultimately replace, petroleum products. Carbohydrates represent the largest fraction of biomass, and several conversion methods such as gasification,^[1–3] pyrolysis,^[4,5] catalytic conversion^[6–9] and fermentation^[10] are under development for the conversion to useful value-added chemicals and fuels. Platform molecules are important in the chemical industry as they are products that can be produced efficiently and selectively in large quantities and used in several other chemical conversions and applications. In the conventional, petroleum based chemical industry, ethylene and benzene are examples of platform molecules.^[11] For a chemical industry based on renewable feedstocks, new platform molecules will be needed.^[12]

Glycolaldehyde (hydroxyacetaldehyde) may be one such platform molecule for a biomass-based chemical industry. Glycolaldehyde can be transformed to other useful chemicals such as ethylene glycol by catalytic hydrogenation,^[13] glycolic acid by mild oxidation,^[14] methyl vinyl glycolate (MVG),^[15–17] and ethanol amines,^[18–20] see Scheme 1.

Glycolaldehyde has previously been identified as a product from pyrolysis of crystalline glucose or lignocellulosic biomass (6–8 % yield).^[21,22] It has also been observed as a major product from

glucose decomposition in supercritical water with yields up to 64 % at 450 °C and 35 MPa,^[23] and by thermal cracking of glucose with yields up to 66 % at 540 °C.^[24] This thermal cracking process is particularly interesting due to its high selectivity and scalability, and it is of interest to further investigate this process with the aim to improve the glycolaldehyde yield and obtain a mechanistic understanding of the process. It is important that the yields are as high as possible to make bio-based processes economically feasible and able to compete with conventional fossil-based processes.

This work studies the thermal cracking process, where sugars are converted to glycolaldehyde and other valuable oxygenates by spraying an aqueous sugar solution into a fluidized bed reactor. The effects of temperature, feed concentration and sugar type are studied, and we propose that glycolaldehyde may function as a renewable platform molecule in future bio-refineries to be used for further conversion to valuable renewable chemicals.

Scheme 1. Glycolaldehyde as a bio-based platform molecule.^[13–17,19,20]

A proposed reaction network for monosaccharide decomposition is shown in Scheme 2. Glucose can be converted to glycolaldehyde through ring-opening, followed by a series of retro-aldol reactions through the C₄ intermediate erythrose. 1,2-ethenediol is formed as an intermediate product, but spontaneously tautomerizes to glycolaldehyde. In principle, glycolaldehyde can be formed from glucose with 100 % atom selectivity. However, in practice several other byproducts and intermediates are observed, mainly other C₁–C₃ oxygenate compounds, see Scheme 2.

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Scheme 2. Proposed reaction network for monosaccharide decomposition to the observed main products.^[25–27] Arrows leaving boxes are retro-aldol reactions.

Figure 1 shows the results of a 90 h glucose cracking experiment. Stable product yields are obtained, with a yield of glycolaldehyde of 72–73 %, and a total carbon balance of 93–95 % in the condensed aqueous product. The high carbon balance suggests that only small amounts of char and permanent gases are formed at these reaction conditions. This was also observed by Majerski et al.,^[24] who found only 0.14 wt% char (based on fed glucose) and 0.51 wt% gases from glucose cracking at 523 °C.^[24] Besides the major product glycolaldehyde, other products include pyruvaldehyde, formaldehyde, glyoxal, acetol and acetic acid. The formation of significant amounts of C₁ and C₃ compounds, such as formaldehyde and pyruvaldehyde, show that other reactions than the direct retro-aldol reaction of glucose occur. This may include isomerization of glucose to fructose prior to retro-aldol reaction, as the direct retro-aldol reaction pathway for glucose produces a C₂ and a C₄ oxygenate (which undergo further retro-aldol reaction to two C₂ oxygenates or, through isomerization to erythrulose, a C₁ and a C₃ oxygenate), as opposed to fructose, which produces two C₃ oxygenates, that may further produce a C₁ and a C₂ species.^[25–27]

Glyoxal, acetol and pyruvaldehyde are also considered valuable products, as they can potentially be hydrogenated to their respective glycols, ethylene glycol and propylene glycol.^[13] Thus, the yield of valuable oxygenates is as high as 86 % when considering glycols production. Acetic acid and formaldehyde

constitute together about 8 %, and are considered lower value products.

Figure 1. Product distribution profile for a 90 h glucose cracking experiment. Reaction conditions: 515 °C, 2.15 g min⁻¹ 20 wt% aqueous glucose solution, 14 NL min⁻¹ N₂, 100 g bed material, vapor residence time ~1 s.

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The influence of operating temperature is shown in Figure 2. The carbon mass balance and glycolaldehyde yield were clearly correlated, and at the optimal temperature of 525 °C, 74 % glycolaldehyde yield and a condensed carbon mass balance of 95 % was achieved. At lower temperatures, the glycolaldehyde and carbon yields were lower, possibly due to increased char formation. For higher temperatures, the glycolaldehyde and carbon balance is reduced, which is likely due to increased gas formation. Majerski et al.^[24] found an increase in the gas formation from 0.51 wt% at 523 °C to 6.15 wt% at 573 °C.

Figure 2. Effect of temperature on glucose cracking. Reaction conditions: 2.15 g min⁻¹ 20 wt% aqueous glucose solution, 14 NL min⁻¹ N₂, 100 g bed material, vapor residence time ~1 s.

The feed concentration is highly influential on the scalability and commercial prospects of the process, as a higher sugar concentration means an increased production capacity and reduced heat requirements for water evaporation, both for the process itself and in any downstream purification.

The glucose concentration was varied in the range 10–60 wt% and the results are shown in Figure 3 (photo of liquid products shown in Supporting Information, Figure S1). The yield of glycolaldehyde was highest at 73–74 % with 20–30 wt% glucose in the feed. At lower glucose concentrations, the glycolaldehyde yield decreased, probably because carbon losses in the setup are relatively higher at lower feed concentration. However, only the yield of glycolaldehyde was lower at 10 % glucose feed concentration, while other products are unchanged or even slightly higher indicating that other effects may be at work too. At higher feed concentrations, the glycolaldehyde yield also decreased with no other observed condensed liquid product significantly increasing. The total carbon balance similarly decreased by 6 percentage points when the feed glucose concentration increased from 40 % to 60 %. An explanation could be that reactions of higher order producing permanent gases and char become more predominant at higher concentrations. It may also be that condensation of the organic compounds became less efficient when the concentration of water was reduced.

The sugar cracking process was also investigated for the monosaccharides fructose and xylose, as well as sucrose, a disaccharide of glucose and fructose. Figure 4 shows that the product distribution significantly depended on the sugar feedstock. As for glucose, the other monosaccharides showed ~93–95 % carbon recovery in the condensed liquid product, with the remaining carbon expected to be char, non-condensable gases and losses in the process.

Figure 3. Effect of glucose concentration on product distribution. Reaction conditions: 515 °C, 2.15 g min⁻¹ aqueous glucose solution, 14 NL min⁻¹ N₂, 100 g bed material, vapor residence time ~1 s.

Glucose showed the highest yield of glycolaldehyde at 73 %, as expected from the cracking pathway shown in Scheme 2, as it can crack to three C₂ oxygenates. The C₅ monosaccharide xylose showed a glycolaldehyde yield of 66 %, with a significantly increased formaldehyde yield of 15 % compared to 7 % for glucose. This is in agreement with the proposed cracking pattern in Scheme 2. Xylose can isomerize to xylulose, and both can crack further to a C₂ (1,2-ethenediol or glycolaldehyde) and a C₃ (glyceraldehyde or prop-1-ene-1,2,3-triol) oxygenate. Glyceraldehyde can further undergo cracking by retro-aldol reaction to a C₁ (formaldehyde) and a C₂ (1,2-ethenediol) oxygenate.

Cracking of fructose yielded only 40 % glycolaldehyde, significantly lower than for glucose and xylose. This is due to the fructose cracking pattern yielding two C₃ components (glyceraldehyde and prop-1-ene-1,2,3-triol), where glyceraldehyde can undergo further cracking to a C₁ and a C₂ oxygenate, while 1,2,3-prop-1-ene-triol can isomerize to dihydroxyacetone (not observed) or further dehydrate to pyruvaldehyde. Comparing cracking of fructose and glucose, the yields of formaldehyde and pyruvaldehyde were especially higher for fructose. However, significant amounts of C₁ and C₃ oxygenates were also produced by cracking of glucose, which may suggest that some glucose isomerizes to fructose prior to retro-aldol reaction steps. Cracking an equal fructose/glucose

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mixture yields similar results as the mean values for glucose and fructose cracked individually, suggesting only limited cross-interaction between different feeds when using 20 % feed solutions. This is especially relevant in an industrial application where it may be desirable to use a pre-hydrolyzed sucrose feed, rather than the pure monosaccharide sugars. Cracking of sucrose was also investigated. While sucrose produced 39 % glycolaldehyde, the total carbon balance was significantly lower than for the monosaccharide sugars. This is likely because ring opening is required for the sugars to undergo the retro-aldol reactions. Sucrose is a non-reducing sugar, thus ring-opening cannot occur before hydrolysis of the glycosidic bond. As the products from sucrose cracking are similar to those from glucose and fructose cracking, although the distribution is different, it is likely that some sucrose hydrolyses under the applied reaction conditions. The significantly lower carbon balance associated with using sucrose as the feed (67 %, compared to 93–95 % for fructose or glucose), is likely due to increased char formation from pathways in competition with sucrose hydrolysis.

Figure 4. Effect of feedstock on product distribution. Reaction conditions: 515 °C, 2.15 g min⁻¹ 20 wt% aqueous sugar solution, 14 NL min⁻¹ N₂, 100 g bed material, vapor residence time ~1 s. Gluc/fruc is an equal glucose/fructose mixture and gluc/fruc calc is the theoretical distribution calculated from the glucose and fructose experiments.

In conclusion, it was shown that sugars in aqueous solutions can be thermally cracked in a fluidized bed of glass beads, and that glucose in particular can be selectively converted to glycolaldehyde with yields as high as 74 %, with up to 95 % carbon recovered in the condensed aqueous product. Stable product composition was observed during continuous operation for more than 90 hours. The process is relevant with respect to a renewable chemical industry, as it provides a scalable process for selectively producing glycolaldehyde in high quantities from biomass feedstocks. Glycolaldehyde may be considered a platform molecule as it can be further converted to a variety of useful chemicals.

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Keywords: biomass • carbohydrates • fast pyrolysis • fluidized bed • retro reactions

Experimental Section

Figure 5. Schematic of the sugar cracking process.

Experiments were carried out in a 41 mm ID fluid bed reactor heated externally using an electric oven and operated at 490–600 °C loaded with 100 g soda lime glass beads (Silibeads SOLID Micro Glass Beads from Sigmund Lindner) with a particle size of 90–150 µm and fluidized by 10 NL min⁻¹ N₂ preheated and fed through a sintered quartz distributor plate. The aqueous 10–60 wt% sugar solutions were fed at ~2.15 g min⁻¹ using a Spraying Systems two-phase spray nozzle with 4 NL min⁻¹ N₂ for atomization. The droplets were rapidly heated, and the vapor residence time was approximately 1 sec. The product vapors were cooled to 220 °C and passed through a cyclone to remove particles and subsequently condensed in a surface condenser at 2–3 °C. The condensed aqueous products were analyzed and quantified using HPLC (for details see Supporting Information, Section 1). The density of the products was measured using an Anton Paar DMA 35 density meter. The uncertainty on the steady-state carbon balance was found to be < 1 % (see Supporting Information, Figures S2–S3 and Table S1). Further experimental details and calculation procedures can be found in Supporting Information, Section 1.

- [1] A. A. Ahmad, N. A. Zawawi, F. H. Kasim, A. Inayat, A. Khasri, *Renew. Sustain. Energy Rev.* **2016**, 53, 1333–1347.
- [2] V. Kirubakaran, V. Sivaramakrishnan, R. Nalini, T. Sekar, M. Premalatha, P. Subramanian, *Renew. Sustain. Energy Rev.* **2009**, 13, 179–186.
- [3] A. Kumar, D. D. Jones, M. A. Hanna, *Energies* **2009**, 2, 556–581.
- [4] A. V. Bridgwater, G. V. C. Peacocke, *Renew. Sustain. energy Rev.* **2000**, 4, 1–73.

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- [5] A. V. Bridgwater, *Biomass and Bioenergy* **2012**, 38, 68–94.
- [6] T. P. Vispute, H. Zhang, A. Sanna, R. Xiao, G. W. Huber, *Science* (80-.) **2010**, 330, 1222–1227.
- [7] M. S. Holm, Y. J. Pagán-Torres, S. Saravanamurugan, A. Riisager, J. A. Dumesic, E. Taarning, *Green Chem.* **2012**, 14, 702–706.
- [8] D. M. Alonso, J. Q. Bond, J. A. Dumesic, *Green Chem.* **2010**, 12, 1493–1513.
- [9] M. S. Holm, S. Saravanamurugan, E. Taarning, *Science* (80-.) **2010**, 328, 602–606.
- [10] Y. Lin, S. Tanaka, *Appl. Microbiol. Biotechnol.* **2006**, 69, 627–642.
- [11] A. Sølvhøj, E. Taarning, R. Madsen, *Green Chem.* **2016**, 18, 5448–5455.
- [12] T. Werpy, G. Petersen, *Volume I - Results of Screening for Potential Candidates from Sugars and Synthesis Gas*, **2004**.
- [13] C. M. Osmundsen, E. Taarning, M. B. Larsen, *Process for the Preparation of Ethylene Glycol from Sugars*, **2017**, US 20170197893A1.
- [14] C. M. Osmundsen, E. Taarning, *A Method and a System for Producing Glycolic Acid and/or Glycolate.*, **2018**, WO 2018/095973 A1.
- [15] M. Dusselier, P. Van Wouwe, S. De Smet, R. De Clercq, L. Verbelen, P. Van Puyvelde, F. E. Du Prez, B. F. Sels, *ACS Catal.* **2013**, 3, 1786–1800.
- [16] R. De Clercq, M. Dusselier, J. Dijkmans, R. I. Iacobescu, Y. Pontikes, B. F. Sels, *ACS Catal.* **2015**, 5, 5803–5811.
- [17] S. Tolborg, S. Meier, S. Saravanamurugan, P. Fristrup, E. Taarning, I. Sádaba, *ChemSusChem* **2016**, 9, 3054–3061.
- [18] W. Faveere, T. T. Mihaylov, M. Pelckmans, K. Moonen, F. G. Hamers, R. Bosschaerts, K. Pierloot, B. F. Sels, *ACS Catal.* **2019**, DOI 10.1021/acscatal.9b02437.
- [19] W. Mägerlein, J.-P. Melder, P. Jörg, J. Eberhardt, T. Krug, M. Kreitschmann, *Reactions of Glycolaldehyde with an Aminating Agent*, **2012**, US20120271068A1.
- [20] G. Liang, A. Wang, L. Li, G. Xu, N. Yan, T. Zhang, *Angew. Chemie - Int. Ed.* **2017**, 56, 3050–3054.
- [21] M. S. Mettler, A. D. Paulsen, D. G. Vlachos, P. J. Dauenhauer, *Green Chem.* **2012**, 14, 1284.
- [22] P. R. Patwardhan, J. A. Satrio, R. C. Brown, B. H. Shanks, *J. Anal. Appl. Pyrolysis* **2009**, 86, 323–330.
- [23] M. Sasaki, K. Goto, K. Tajima, T. Adschiri, K. Arai, *Green Chem.* **2002**, 4, 285–287.
- [24] P. A. Majerski, J. K. Piskorz, D. S. A. G. Radlein, *Production of Glycolaldehyde by Hydrous Thermolysis of Sugars*, **2002**, US 7094932B2.
- [25] J. B. Paine, Y. B. Pithawalla, J. D. Naworal, *J. Anal. Appl. Pyrolysis* **2008**, 82, 42–69.
- [26] V. Seshadri, P. R. Westmoreland, *J. Phys. Chem. A* **2012**, 116, 11997–12013.
- [27] J. B. Paine, Y. B. Pithawalla, J. D. Naworal, *J. Anal. Appl. Pyrolysis* **2008**, 82, 10–41.

Graphical abstract

Glucose can be selectively converted to glycolaldehyde by a thermal cracking process with principally 100 % atom efficiency. Glycolaldehyde may function as a renewable platform molecule for further conversion to ethylene glycol and other valuable chemicals. In this work, 74 % glycolaldehyde yield is demonstrated and the effect of operating conditions are investigated.